Light-driven molecular motors

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Light-Driven Molecular Motors; Stepwise Thermal Helix Inversion During Unidirectional Rotation of Sterically Overcrowded Biphenanthrylidenes

Supporting Information

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A Experimental Section

2,3-Dihydro-3,7-dimethyl-4(1*H*)-phenanthrenone (7)

This ketone was prepared starting from ketone **6** (3.0 g, 14.2 mmol) following the procedure for the methylation of ester **10**. The product (3.09 g, 13.8 mmol, 97%) was obtained as a slightly yellow, sticky solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30-1.32 (d, J = 7.0 Hz, 3H), 1.90-2.03 (dq, J = 11.7, 5.1 Hz, 1H), 2.21-2.30 (m, 1H), 2.50 (s, 3H), 2.69-2.81 (m, 1H), 3.06-3.26 (m, 2H), 7.24-7.27 (d, J = 8.4 Hz, 1H), 7.43-7.46 (dd, J = 8.8, 1.8 Hz, 1H), 7.57 (s, 1H), 7.81-7.84 (d, J = 8.4 Hz, 1H), 9.23-9.26 (d, J = 8.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.9 (q), 21.2 (q), 30.2 (t), 31.2 (t), 43.8 (d), 126.2 (d), 126.8 (d), 127.0 (d), 127.2 (d), 129.4 (s), 130.7 (d), 132.9 (s), 133.2 (d), 135.2 (s), 144.9 (s), 203.4 (s); *m/z* (EI, %) = 225 (15), 224 (M^+, 88), 182 (100), 154 (51), 153 (27), 152 (15); HRMS (EI): calcd. for $C_{16}H_{16}O$: 224.1211, found 224.1201.

4-(6-Methyl-naphthalen-2-yl)-butyric acid methyl ester (8)

To a solution of 4-(6-methyl-naphthalen-2-yl)-butyric acid **5** (2.8, 0.35 g, 1.5 mmol) in 25 ml of methanol was added 0.4 ml of concentrated sulfuric acid. This mixture was refluxed overnight (12 h) and then poured into a sat. aq. sol. of $NaHCO_3$ (100 ml). The water layer was extracted with ether (3x 100 ml). The combined organic layers were washed with brine (2x 100ml), dried ($MgSO_4$) and filtered. Finally, the organic volatiles were removed under reduced pressure yielding a white solid (0.35 g, 1.44 mmol, 96%). If required, further purification can be achieved by column chromatography (SiO_2, hexane:ethyl acetate= 2:1, R_f= 0.8); m.p. 45.0-45.2°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.01-2.09 (m, 2H), 2.34-2.39 (t, J= 7.3 Hz, 2H), 2.50 (s, 3H), 2.77-2.82 (t, J= 7.7 Hz, 2H), 3.66 (s, 3H), 7.27-7.30 (m, 2H), 7.57 (s, 2H), 7.66-7.70 (dd, J= 8.4, 2.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6 (q), 26.3 (t), 33.3 (t), 35.1 (t), 51.4 (q), 126.3 (d), 126.5 (d), 127.2 (d), 127.3 (d), 128.1 (d), 131.7 (d), 132.2 (s), 134.7 (s), 137.8 (s), 150.9 (s), 173.9 (s); *m/z* (EI, %) = 242 (M^+, 58), 168 (100), 155 (51); HRMS (EI):

calcd. for $C_{16}H_{18}O_2$: 242.1307, found 242.1308; Ele. anal., calc. (%): C, 79.31; H, 7.49; found (%): C, 79.32; H, 7.58.

2-Ethyl-4-(6-methyl-naphthalen-2-yl)-butyric acid methyl ester (9)

This compound was prepared following the procedure for ester **10**. Starting from ester **8** (3.0 g, 12.4 mmol), the desired product **9** was obtained as a colorless oil (2.63 g, 10.2 mmol, 82%) after column chromatography (SiO_2, hexane: ethyl acetate=50:1, R_f=0.26); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87-0.92 (t, J=7.5 Hz, 3H), 1.43-1.73 (m, 2H), 1.78-1.89 (m, 1H), 1.98-2.11 (m, 1H), 2.32-2.42 (m, 1H), 2.49 (s, 3H), 2.67-2.79 (m, 2H), 3.69 (s, 3H), 7.26-7.29 (m, 2H), 7.56-7.57 (m, 2H), 7.66-7.69 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.5 (q), 21.4 (q), 25.3 (t), 33.4 (t), 33.6 (t), 46.5 (d), 51.1 (q), 126.0 (d), 126.4 (d), 127.02 (d), 127.06 (d), 127.08 (d), 127.9 (d), 131.7 (s), 132.1 (s), 134.4 (s), 138.0 (s), 176.2 (s); *m/z* (EI, %) = 270 (M^+, 60), 169 (32) 168 (100), 155 (48); HRMS (EI): calcd. for $C_{18}H_{22}O$: 270.1620, found 270.1593; Ele. anal., calc. (%): C, 79.96; H 8.20; found: C, 79.66; H, 8.30.

3-Methyl-2-[2-(6-methyl-naphthalen-2-yl)-ethyl]-butyric acid methyl ester (10)

To a solution of *i*-Pr_2NH (0.6 ml, 0.43 g, 4,3 mmol) in THF (10 ml) was added at –60°C a solution of *n*-BuLi in *n*-hexane (2.6 ml, 4.2 mmol). The resulting yellow solution was stirred for 15 min. Subsequently, a solution of ester **8** (0.92 g, 3.8 mmol) in THF (20 ml) was added dropwise at –60°C. The yellow solution was stirred for 1h at –60°C. Then *i*-propyl iodide (0.4 ml, 5.2 mmol) was added, whereupon the reaction mixture was stirred overnight. The reaction was quenched with addition of a sat. aq. sol. of NH_4Cl (50 ml). The reaction mixture was extracted with ether (3x 50 ml) and the combined organic layers were washed with brine. Drying over $MgSO_4$ and removal of the solvent under reduced pressure gave a colorless oil which was purified using column chromatography (SiO_2, hexane:ethyl acetate = 16:1, R_f=0.6) yielding a colorless oil which solidified upon standing (0.65 g, 2.3 mmol, 60%); m.p. 65-66˚C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86-0.92 (d, J= 6.6 Hz, 3H), 0.91-0.93 (d,

J= 6.6 Hz, 3H), 1.82-1.95 (m, 2H), 1.96-2.09 (m, 1H), 2.19-2.26 (m, 1H), 2.49 (s, 3H), 2.58-2.80 (m, 2H), 3.70 (s, 3H), 7.27-7.29 (d, *J*= 8.4 Hz, 2H), 7.55-7.57 (d, *J*= 4.0 Hz, 2H), 7.66-7.69 (d, *J*= 8.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.0 (q), 20.2 (q), 21.4 (q), 30.5 (d), 31.2 (t), 34.0 (t), 50.8 (q), 51.9 (d), 126.0 (d), 126.4 (d), 127.0 (d), 127.1 (d), 127.1 (d), 127.9 (d), 131.7 (s), 132.1 (s), 134.3 (s), 138.1 (s), 175.7 (s); *m/z* (EI, %) = 284 (M^+, 51), 168 (100), 155 (46); HRMS (EI): calcd. for $C_{19}H_{24}O_2$: 284.1776, found 284.1764; Ele. anal., calc. (%): C, 80.24; H, 8.51; found: C, 80.57; H, 8.57.

2-Ethyl-4-(6-methyl-naphthalen-2-yl)-butyric acid (11)

This compound was prepared starting from **9** (8.53 g, 31 mmol) in the same way as compound **12** and was obtained as a colorless oil (7.89 g, 30.8 mmol, 98%); ^{1}H (300 MHz, $CDCl_3$) δ 0.96-1.00 (t, *J*=7.3 Hz, 3H), 1.61-1.83 (m, 2H), 1.85-1.95 (m, 1H), 2.04-2.16 (m, 1H), 2.37-2.46 (m, 1H), 2.51 (s, 3H), 2.73-2.91 (m, 2H), 7.28-7.33 (m, 2H), 7.58-7.60 (m, 2H), 7.68-7.71 (m, 2H); ^{13}C (75 MHz, $CDCl_3$) δ 11.6 (q), 21.6 (q), 25.2 (t), 33.2 (t), 33.6 (t), 46.5 (d), 126.2 (d), 126.5 (d), 127.2 (d), 127.2 (d), 127.3 (d), 128.1 (d), 131.8 (s), 132.2 (s), 134.6 (s), 138.0 (s), 183.0 (s); *m/z* (EI, %) = 256 (M^+, 48), 169 (35), 168 (100), 155 (68); HRMS (EI): calcd. for $C_{17}H_{20}O_2$: 256.1463, found 256.1457; Ele. anal., calc. (%): C, 79.65; H, 7.86; found (%): C, 79.44; H, 7.91.

3-Methyl-2-[2-(6-methyl-naphthalen-2-yl)-ethyl]-butyric acid (12)

A mixture of ester **10** (1.31 g, 4.60 mmol), ethanol (20 ml), water (20 ml) and KOH (2.5 g, 44 mmol) was refluxed during 8h. After cooling to room temperature, the mixture was acidified with an aq. sol. of 10% HCl (100 ml) and extracted with CH_2Cl_2 (3x 50 ml). The combined organic layers were washed with water, dried on Na_2SO_4 and the solvent removed under reduced pressure giving a slightly colored oil which solidified upon standing (1.21 g, 4.48 mmol, 97%); m.p. 82.6-82.7°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96-0.98 (d, *J*=6.6 Hz, 3H), 0.97-0.99 (d, *J*= 6.6 Hz, 3H), 1.83-2.11 (m, 3H), 2.23-2.30 (m, 1H), 2.49 (s, 3H), 2.64-2.74 (m, 1H), 2.81-2.91 (m, 1H), 7.27-7.31 (m, 2H), 7.58 (s, 2H), 7.67-7.70 (d,

J= 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.0 (q), 20.4 (q), 21.6 (q), 30.5 (d), 30.9 (t), 34.1 (t), 51.9 (d), 126.2 (d), 126.3 (d), 126.5 (d), 127.2 (d), 127.2 (d), 128.2 (d), 131.8 (s), 132.2 (s), 134.7 (s), 138.2 (s), 182.1 (s); *m/z* (EI, %) = 270 (M^+, 48), 168 (100), 155 (69); HRMS (EI): calcd. for $C_{18}H_{22}O_2$: 270.1620, found 270.1606; Ele. anal., calc. (%): C, 79.96; H, 8.20; found (%): C, 79.83; H, 8.22.

3-Ethyl-7-methyl-2,3-dihydro-4(1*H*)-phenanthrenone (13)

This compound was prepared starting from **11** (0.85 g, 3.4 mmol) in the same way as compound **14** and was obtained as a colorless oil (0.60 g, 2.5 mmol, 74%) after column chromatography (SiO_2, hexane:ethyl acetate= 50:1, R_f= 0.36); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.01-1.04 (t, *J*=7.3 Hz, 3H), 1.56-1.66 (m, 1H), 1.89-2.07 (m, 2H), 2.25-2.34 (m, 1H), 2.50 (s, 3H), 2.50-2.60 (m, 1H), 3.10-3.14 (dd, *J*= 7.1 Hz, 5.3 Hz, 2H), 7.23-7.26 (d, *J*= 8.4 Hz, 1H), 7.43-7.47 (dd, *J*= 8.8 Hz, 1.6, Hz, 1H), 7.57 (s, 1H), 7.80-7.83 (d, 8.4 Hz, 1H), 9.20-9.23 (d, *J*= 8.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.6 (q), 21.2 (q), 23.1 (t), 27.7 (t), 29.7 (t), 50.4 (d), 126.2 (d), 126.8 (d), 127.3 (d), 127.4 (s), 129.4 (s), 130.7 (d), 133.0 (s), 133.1 (d), 135.5 (s), 144.6 (s), 203.2 (s); *m/z* (EI, %) = 238 (M^+, 70), 210 (100), 182 (62), 154 (56); HRMS (EI): calcd. for $C_{17}H_{18}O$: 238.1358, found 238.1363.

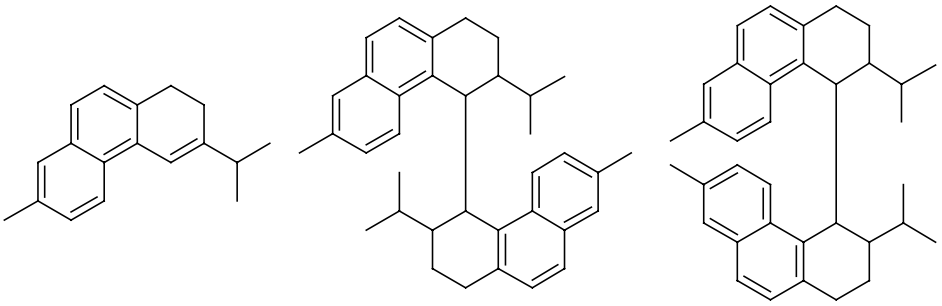
3-*i*-Propyl-7-methyl-2,3-dihydro-4(1*H*)-phenanthrenone (14)

A solution of **12** (1.21 g, 4.48 mmol) in toluene (50 ml) was stirred together with PCl_5 (1.15 g, 5.5 mmol) at room temperature for 2 h. The reaction mixture was placed in an ice bath and $SnCl_4$ (1.3 ml, 11 mmol) was added and stirring was continued for 3h at 0°C. An aq. sol of 1*N* NaOH (100 ml) was added and the mixture was extracted with CH_2Cl_2 (3x 50 ml). The combined organic layers were dried ($MgSO_4$) and the solvent removed under reduced pressure. The product was purified using column chromotography (SiO_2, hexane:ethyl acetate=16:1, R_f=0.65) giving a colorless oil (0.73 g, 2.90 mmol, 65%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94-0.96 (d, *J*= 6.2 Hz, 3H), 0.99-1.01 (d, *J*= 6.2 Hz, 3H), 2.02-2.09 (m, 1H), 2.18-2.28 (m, 1H), 2.41-2.47 (m, 2H), 2.50 (s, 3H), 2.99-3.19 (m, 2H), 7.24-7.26 (d, *J*=

8.2 Hz, 1H), 7.43-7.46 (d, *J*= 9.0 Hz, 1H), 7.57 (s, 1H), 7.80-7.83 (d, *J*= 8.2 Hz, 1H), 9.08-9.11 (d, *J*= 9.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.8 (q), 20.9 (q), 21.2 (q), 23.4 (t), 27.3 (d), 29.2 (t), 55.3 (d), 126.0 (d), 126.6 (d), 127.2 (d), 127.9 (s), 129.2 (s), 130.6 (d), 132.9 (d), 133.0 (s), 135.2 (s), 144.3 (s), 203.5 (s); *m/z* (EI, %) = 252 (M^+, 61), 237 (21), 210 (100), 209 (23), 182 (36), 154 (34); HRMS (EI): calcd. for $C_{18}H_{20}O$: 252.1514, found 252.1519; Ele. anal., calc. (%): C, 85.67; H, 7.99; found (%): C, 85.00; H, 8.15.

B Side products obtained from the McMurry reaction with ketone 4.

In the reaction of ketone **4** with $TiCl_4$ and zinc powder, three apolar side products (**15**, **16** and **17**) were separated and characterized. As is postulated in studies by Ephritikhine *et al*., these compounds might have been formed from reactive intermediates in the reaction mixture such as titanium alkylidene species.[1]



15 **16** **17**

Figure S1. Apolar side-products obtained from the McMurry coupling reaction of ketone **14**.

3-*i*-Propyl-7-methyl-1,2-dihydrophenanthrene (15)

This compound was obtained as a side product in the McMurry reaction in the synthesis of olefin **4** and was obtained as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19-1.21 (d, J=6.6 Hz, 6H), 2.28-2.34 (t, J= 8.2 Hz, 2H), 2.49 (s, 3H), 2.54-2.61 (m, 1H), 2.88-2.93 (d, J= 8.2 Hz, 2H), 6.99 (s, 1H), 7.23-7.25 (d, J= 8.1 Hz, 1H), 7.28-7.32 (dd, J= 8.8, 1.5 Hz, 1H), 7.49-7.54 (m, 2H), 8.01-8.04 (d, J= 8.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2 (2xq), 25.2 (t), 29.3 (t), 35.7 (d), 115.2 (d), 122.3 (d), 125.2 (d), 126.5 (d), 127.4 (d), 127.6 (s), 127.8 (d), 129.5 (s), 131.0 (s), 133.1 (s), 134.0 (s), 148.8 (s); *m/z* (EI, %) =236 (M^+, 95), 221 (100); HRMS (EI): calcd. for $C_{18}H_{20}$: 236.1565, found 236.1555.

***Trans*-1,1',2,2',3,3',4,4'-Octahydro-3,3'-di-*i*-propyl-7,7'-dimethyl-4,4'-biphenanthrene (16)**

This compound was obtained as a side product in the McMurry reaction in the synthesis of olefin **4** and was obtained as a white powder; 210.8-212.2°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.68-0.71 (d, *J*= 6.6 Hz, 6H), 0.73-0.76 (d, *J*= 6.6 Hz, 6H), 1.32-1.52 (m, 6H), 1.91-1.95 (m, 2H), 2.47 (s, 6H), 2.55-2.68 (m, 4H), 3.90 (s, 2H), 7.06-7.08 (m, 4H), 7.43-7.46 (d, *J*= 8.4 Hz, 2H), 7.53-7.56 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.2 (q), 21.2 (q), 21.3 (q), 21.6 (t), 27.4 (t), 30.9 (d), 42.1 (d), 43.5 (d), 123.6 (d), 125.3 (d), 127.3 (d), 127.6 (d), 127.7 (d), 131.7 (s), 132.8 (s), 133.5 (s), 134 .8 (s), 135.5 (s); *m/z* (EI, %) = 475 (0.2), 474 (M^+, 0.6), 473 (0.2), 472 (0.4), 238 (22), 237 (100), 236 (27), 181 (73); HRMS (EI): calcd. for $C_{36}H_{42}$: 474.3287, found 474.3269.

***Cis*-1,1',2,2',3,3',4,4'-Octahydro-3,3'-di-*i*-propyl-7,7'-dimethyl-4,4'-biphenanthrene (17)**

This compound was obtained as a side product in the McMurry reaction in the synthesis of olefin **4** and was obtained as a white powder; m.p. 174.8-176.2°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.78-0.80 (d, *J*= 6.2 Hz, 6H), 0.94-0.96 (d, *J*= 6.6 Hz, 6 Hz), 1.27-1.35 (m, 2H), 1.93-2.09 (m, 4H), 2.15 (s, 6H), 2.31-2.42 (m, 2H), 2.93-3.05 (m, 2H), 3.15-3.24 (m, 2H), 3.72 (s, 2H), 6.36-6.38 (d, *J*= 8.6 Hz, 2H), 6.57-6.60 (d, *J*= 8.6 Hz, 2H), 6.88 (s, 2H), 7.00-7.02 (d, *J*= 8.4 Hz, 2H), 7.15-7.18 (d, *J*= 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.0 (t), 20.9 (q), 21.36 (q), 21.42 (q), 26.0 (t), 28.1 (d), 39.7 (d), 40.3 (d), 120.9 (d), 125.0 (d), 125.8 (2xd), 126.9 (d), 131.0 (s), 131.5 (s), 132.1 (s), 132.8 (s), 133.9 (s); *m/z* (EI, %) = 475 (2.2), 474 (M^+, 5.3), 473 (0.7), 472 (1.2), 238 (21), 237 (100), 236 (25), 181 (60); HRMS (EI): calcd. for $C_{36}H_{42}$: 474.3287, found 474.3270.

C X-ray Analyses

C1. (3*S*,3'*S*)-(*M**,*M**)-*trans*-2

The crystal structure of (3*S*,3'*S*)-(*M*,*M*)-*trans*-**2** has been published previously.[2]

Table S1. Relevant bond lengths, angles and torsion angles for (3*S*,3'*S*)-(*M*,*M*)-*trans*-**2**.

bond lengths (Å):	
C_4-$C_{4'}$	1.345(3)
angles (°):	
C_3-C_4-C_{4a}	111.27(17)
C_3-C_4-$C_{4'}$	123.5(2)
C_{4a}-C_4-$C_{4'}$	124.31(19)
plane naphthalenes[3]	62.71(7)
torsion angles (°):	
C_3-C_4-$C_{4'}$-$C_{3'}$	158.3(2)
C_3-C_4-$C_{4'}$-$C_{4'a}$	-9.8(3)
$C_{3'}$-$C_{4'}$-C_4-C_{4a}	-9.8(3)
C_{4a}-C_4-$C_{4'}$-$C_{4'a}$	-177.93(19)
$C_{4'}$-C_4-C_3-C_{3ax}	131.7(3)
C_{4b}-C_{4a}-C_4-$C_{4'}$	-60.7(3)

Table S2. X-ray crystallographic data of (3*S*,3'*S*)-(*M*,*M*)-*trans*-(+)-**2**

formula	$C_{32}H_{32}$
fw ($g \cdot mol^{-1}$)	416.60
crystal dimension (mm)	0.18 x 0.20 x 0.25
color	colorless
habit	parallelepiped
crystal system	orthorhombic
space group, no.	$P2_12_12$, 18
a (Å)	9.042(1)
b (Å)	18.855(1)
c (Å)	6.767(1)
β (°)	
V ($Å^3$)	1153.7(2)
Z	2
ρ ($g \cdot cm^{-3}$)	1.199
T (K)	130
μ (cm^{-1})	0.67
number of reflections	1452
number of refined parameters	209
final agreement factors:	
$wR(F^2)$	0.1005
$R(F)$	0.0390
GooF	1.005

C2. (3*R**,3'*R**)-(*P**,*P**)-*trans*-3

The crystals of racemic (3*R**,3'*R**)-(*P**,*P**)-*trans*-**3** suitable for X-ray analysis were obtained by recrystallization from *n*-hexane.

Table S3. Relevant bond lengths, angles and torsion angles for (3*R**,3'*R**)-(*P**,*P**)-*trans*-**3**.

bond lengths (Å):	
C_4-$C_{4'}$	1.3414(19)
angles (°):	
C_3-C_4-C_{4a}	111.05(11)
C_3-C_4-$C_{4'}$	123.82(12)
C_{4a}-C_4-$C_{4'}$	124.42(11)
plane naphthalenes[3]	56.56(4)
torsion angles (°):	
C_3-C_4-$C_{4'}$-$C_{3'}$	-173.58(11)
C_3-C_4-$C_{4'}$-$C_{4'a}$	-4.10(18)
$C_{3'}$-$C_{4'}$-C_4-C_{4a}	-4.10(18)
C_{4a}-C_4-$C_{4'}$-$C_{4'a}$	165.37(11)
$C_{4'}$-C_4-C_3-C_{3ax}	-122.23(13)
C_{4b}-C_{4a}-C_4-$C_{4'}$	66.39(17)

Table S4. X-ray crystallographic data of (3*R**,3'*R**)-(*P**,*P**)-*trans*-(±)-**3**.

formula	$C_{34}H_{36}$
fw ($g \cdot mol^{-1}$)	444.66
crystal dimension (mm)	0.42 x 0.39 x 0.35
color	colorless
habit	block
crystal system	monoclinic
space group, no.	*C*2/c, 15
a (Å)	18.841(1)
b (Å)	6.9763(4)
c (Å)	20.604(1)
β (°)	112.187(1)
V ($Å^3$)	2507.7(2)
Z	4
ρ ($g \cdot cm^{-3}$)	1.178
T (K)	100(1)
μ (cm^{-1})	0.66
number of reflections	2572
number of refined parameters	226
final agreement factors:	
$wR(F^2)$	0.1331
$R(F)$	0.0465
GooF	1.06

C3. (3*S**,3'*S**)-(*P**,*P**)-*trans*-4

The crystals of racemic suitable for X-ray analysis were obtained by recrystallization from heptane.

Table S5. Relevant bond lengths, angles and torsion angles for (3*S**,3'*S**)-(*P**,*P**)-*trans*-**4**.

	residue 1:	residue 2:
bond lengths (Å):		
C_4-$C_{4'}$	1.355(3)	1.347(4)
angles (°):		
C_3-C_4-C_{4a}	111.22(3)	110.8(3)
C_3-C_4-$C_{4'}$	122.76(17)	123.0(3)
C_{4a}-C_4-$C_{4'}$	123.18(18)	124.5(3)
plane naphthalenes[3]	54.59(8)	50.44(10)
torsion angles (°):		
C_3-C_4-$C_{4'}$-$C_{3'}$	-146.48(18)	159.2(3)
C_3-C_4-$C_{4'}$-$C_{4'a}$	12.8(3)	-4.6(4)
$C_{3'}$-$C_{4'}$-C_4-C_{4a}	12.8(3)	-4.6(4)
C_{4a}-C_4-$C_{4'}$-$C_{4'a}$	172.01(17)	-168.4(2)
$C_{4'}$-C_4-C_3-C_{3ax}	-145.44(18)	152.6(3)
C_{4b}-C_{4a}-C_4-$C_{4'}$	65.5(3)	-69.6(4)

Table S6. X-ray crystallographic data of (3*S**,3'*S**)-(*P**,*P**)-*trans*-(±)-**4**.

formula	$C_{36}H_{40}$
fw (g·mol^{-1})	472.71
crystal dimension (mm)	0.40 x 0.20 x 0.04
color	colorless
habit	plate
crystal system	monoclinic
space group, no.	*P*2/a, 13
a (Å)	18.161 (2)
b (Å)	7.3428(7)
c (Å)	22.132(2)
β (°)	113.698(2)
V (Å^3)	2702.5(5)
Z	4
ρ (g·cm^{-3})	1.162
T (K)	110(2)
μ (cm^{-1})	0.65
number of reflections	4755
number of refined parameters	489
final agreement factors:	
wR(F^2)	0.1278
R(*F*)	0.0507
GooF	1.02

C4. (3R^*,3'R^*)-(P^*,P^*)-*cis*-2

Suitable crystals of (3R^*,3'R^*)-(P^*,P^*)-*cis*-**2** were obtained by recrystallization from heptane.

Table S7. Relevant bond lengths, angles and torsion angles for the stable *cis*-alkenes **2**.

bond lengths (Å):	
C_4-$C_{4'}$	1.347(3)
angles (°):	
C_3-C_4-C_{4a}	112.92(17)
C_3-C_4-$C_{4'}$	122.34(19)
C_{4a}-C_4-$C_{4'}$	124.67(19)
$C_{3'}$-$C_{4'}$-$C_{4'a}$	112.95(17)
$C_{3'}$-$C_{4'}$-C_4	122.41(19)
$C_{4'a}$-$C_{4'}$-$C_{4'}$	124.60(19)
plane naphthalenes[3]	48.23(7)
torsion angles (°):	
C_3-C_4-$C_{4'}$-$C_{3'}$	5.5(3)
C_3-C_4-$C_{4'}$-$C_{4'a}$	-176.9(2)
$C_{3'}$-$C_{4'}$-C_4-C_{4a}	-177.8(2)
C_{4a}-C_4-$C_{4'}$-$C_{4'a}$	-0.2(3)
$C_{4'}$-C_4-C_3-C_{3ax}	-97.4(3)
C_4-$C_{4'}$-$C_{3'}$-$C_{3'ax}$	-96.3(3)
C_{4b}-C_{4a}-C_4-$C_{4'}$	54.0(3)
$C_{4'b}$-$C_{4'a}$-$C_{4'}$-C_4	53.1(3)

Table S8. X-ray crystallographic data of (3R^*,3'R^*)-(P^*,P^*)-*cis*-(±)-**2**.

compound	stable *cis*-(±)-**2**

formula	$C_{32}H_{32}$
fw (g·mol-1)	416.60
crystal dimension (mm)	0.25 x 0.22 x 0.17
color	colorless
habit	block
crystal system	orthorhombic
space group, no.	*Pbca*, 61
a (Å)	11.736(3)
b (Å)	16.546(4)
c (Å)	24.984(5)
V (Å^3)	4851(2)
Z	8
ρ (g·cm^{-3})	1.141
T (K)	297(1)
μ (cm^{-1})	0.64
number of reflections	4277
number of refined parameters	417
final agreement factors:	
wR(F^2)	0.1391
R(*F*)	0.0514
GooF	1.002

C5. (3*R**,3'*R**)-(*P**,*P**)-*cis*-3

Suitable crystals of (3*R**,3'*R**)-(*P**,*P**)-*cis*-**3** were obtained by recrystallization from ethanol.

Table S9. Relevant bond lengths, angles and torsion angles for the stable *cis*-alkene **3**.

bond lengths (Å):	
C_4-$C_{4'}$	1.352(2)
angles (°):	
C_3-C_4-C_{4a}	112.85(12)
C_3-C_4-$C_{4'}$	123.07(13)
C_{4a}-C_4-$C_{4'}$	124.04(14)
$C_{3'}$-$C_{4'}$-$C_{4'a}$	112.70(12)
$C_{3'}$-$C_{4'}$-C_4	123.08(13)
$C_{4'a}$-$C_{4'}$-$C_{4'}$	124.13(14)
plane naphthalenes[3]	48.91(5)
torsion angles (°):	
C_3-C_4-$C_{4'}$-$C_{3'}$	4.5(2)
C_3-C_4-$C_{4'}$-$C_{4'a}$	-179.25(14)
$C_{3'}$-$C_{4'}$-C_4-C_{4a}	-177.94(14)
C_{4a}-C_4-$C_{4'}$-$C_{4'a}$	-1.7(2)
$C_{4'}$-C_4-C_3-C_{3ax}	-96.30(17)
C_4-$C_{4'}$-$C_{3'}$-$C_{3'ax}$	-102.08(17)
C_{4b}-C_{4a}-C_4-$C_{4'}$	54.6(2)
$C_{4'b}$-$C_{4'a}$-$C_{4'}$-C_4	55.6(2)

Table S10. X-ray crystallographic data of (3*R**,3'*R**)-(*P**,*P**)-*cis*-(±)-**3**.

formula	$C_{34}H_{36}$
fw (g·mol-1)	444.66
crystal dimension (mm)	0.42 x 0.11 x 0.07
color	colorless
habit	platelet
crystal system	orthorhombic
space group, no.	*Pbca*, 61
a (Å)	11.8625(6)
b (Å)	16.6360(8)
c (Å)	25.452(1)
V (Å^3)	5022.8(4)
Z	8
ρ (g·cm^{-3})	1.176
T (K)	100(1)
μ (cm^{-1})	0.66
number of reflections	5539
number of refined parameters	451
final agreement factors:	
wR(F^2)	0.1132
R(*F*)	0.0474
GooF	1.032

C6. (3*R**,3'*R**)-(*P**,*P**)-*trans*-4

Table S11. Relevant angles and torsion angles of (3*R**,3'*R**)-(*P**,*P**)-*trans*-**4**.

angles:	(°)	torsion angles:	(°)
C_3-C_4-C_{4a}	114.23(16)	C_3-C_4-$C_{4'}$-$C_{3'}$	-157.38(19)
C_3-C_4-$C_{4'}$	124.35(18)	C_3-C_4-$C_{4'}$-$C_{4'a}$	22.1(3)
C_{4a}-C_4-$C_{4'}$	121.41(19)	$C_{3'}$-$C_{4'}$-C_4-C_{4a}	21.7(3)
$C_{3'}$-$C_{4'}$-$C_{4'a}$	114.07(16)	C_{4a}-C_4-$C_{4'}$-$C_{4'a}$	-158.77(19)
$C_{3'}$-$C_{4'}$-C_4	124.71(19)	$C_{4'}$-C_4-C_3-C_{3eq}	30.5(3)
$C_{4'a}$-$C_{4'}$-C_4	121.2(2)	C_4-$C_{4'}$-$C_{3'}$-$C_{3'eq}$	29.7(3)
plane		C_{4b}-C_{4a}-C_4-$C_{4'}$	48.6(3)
naphthalenes[2]	72.81(8)	$C_{4'b}$-$C_{4'a}$-$C_{4'}$-C_4	49.0(3)

Table S12. X-ray crystallographic data of (3*R**,3'*R**)-(*P**,*P**)-*trans*-(±)-**4**.

formula	$C_{36}H_{40}$
fw (g·mol-1)	472.71
crystal dimension (mm)	0.44 x 0.34 x 0.21
color	light-yellow
habit	block
crystal system	triclinic
space group, no.	*P*-1, 2
a (Å)	9.523(4)
b (Å)	12.352(5)
c (Å)	13.559(5)
α (°)	63.298(6)
β (°)	77.596(7)
γ (°)	76.146(6)
V (Å^3)	1372.8(10)
Z	2
ρ (g·cm^{-3})	1.144
T (K)	100(1)
μ (cm^{-1})	0.64
number of reflections	4917
number of refined parameters	485
final agreement factors:	
wR(F^2)	0.1829
R(*F*)	0.0563
GooF	1.034

C7. (3*S**,3'*S**)-(*P**,*M**)-*trans*-4

A suitable crystal of (3*S**,3'*S**)-(*P**,*M**)-*trans*-(±)-**4** was obtained by recrystallization from heptane. For numbering convenience, the carbon atom of the double bond in the half of the molecule with the (3*S**)-(*P**) relative chirality is arbitrarily assigned to be C_4. The other carbon atom of the double bond in the half with the relative (3*S**)-(*M**) stereochemistry is arbitrarily assigned to be $C_{4'}$.

Table S13. Relevant angles and torsion angles of (3*S**,3'*S**)-(*P**,*M**)-*trans*-**4**.

angles:	(°)	torsion angles:	(°)
C_3-C_4-C_{4a}	116.58(18)	C_3-C_4-$C_{4'}$-$C_{3'}$	-162.4(3)
C_3-C_4-$C_{4'}$	116.64(19)	C_3-C_4-$C_{4'}$-$C_{4'a}$	16.5(3)
C_{4a}-C_4-$C_{4'}$	124.84(14)	$C_{3'}$-$C_{4'}$-C_4-C_{4a}	1.2(4)
$C_{3'}$-$C_{4'}$-$C_{4'a}$	98.58(19)	C_{4a}-C_4-$C_{4'}$-$C_{4'a}$	179.98(17)
$C_{3'}$-$C_{4'}$-C_4	136.6(2)	$C_{4'}$-C_4-C_3-C_{3ax}	-114.6(3)
$C_{4'a}$-$C_{4'}$-C_4	124.84(14)	C_4-$C_{4'}$-$C_{3'}$-$C_{3'eq}$	18.7(5)
plane		C_{4b}-C_{4a}-C_4-$C_{4'}$	70.5(2)
naphthalenes[2]	parallel, 0.0	$C_{4'b}$-$C_{4'a}$-$C_{4'}$-C_4	-70.5(2)

Table S14. X-ray crystallographic data of (3*S**,3'*S**)-(*P**,*M**)-*trans*-(±)-**4**.

formula	$C_{36}H_{40}$
fw (g·mol-1)	472.71
crystal dimension (mm)	0.53 x 0.15 x 0.12
color	colorless
habit	prisma
crystal system	triclinic
space group, no.	*P*-1, 2
a (Å)	7.7179(7)
b (Å)	8.5901(8)
c (Å)	10.957(1)
α (°)	81.449(2)
β (°)	80.396(2)
γ (°)	72.358(2)
V (Å^3)	678.82(11)
Z	1
ρ (g·cm^{-3})	1.156
T (K)	100 (1)
μ (cm^{-1})	0.65
number of reflections	3006
number of refined parameters	254
final agreement factors:	
wR(F^2)	0.1535
R(*F*)	0.0534
GooF	1.098

D Eyring Plots

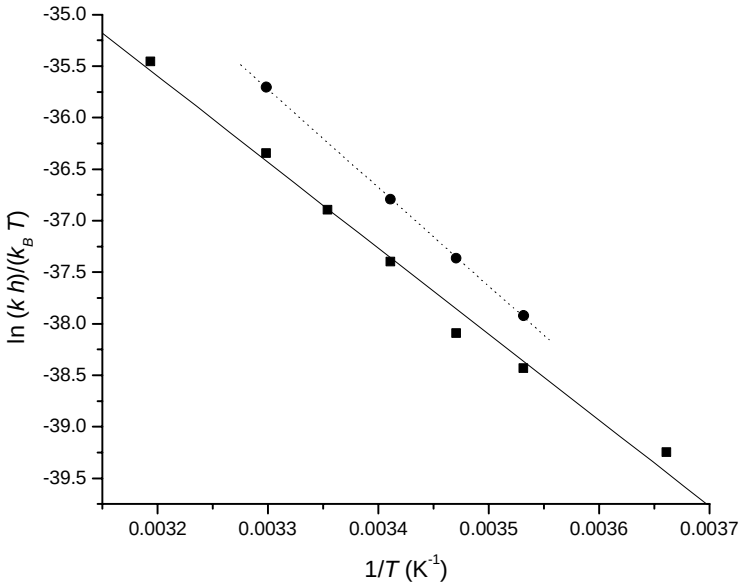


Figure S2. Eyring plots thermal helix inversion of (3*S*,3'*S*)-(*P*,*P*)-*cis*-**2** to (3*S*,3'*S*)-(*M*,*M*)-*cis*-**2** (solid line, squares) and (3*R*,3'*R*)-(*M*,*M*)-*cis*-**3** to (3*R*,3'*R*)-(*P*,*P*)-*cis*-**3** (dotted line, circles).

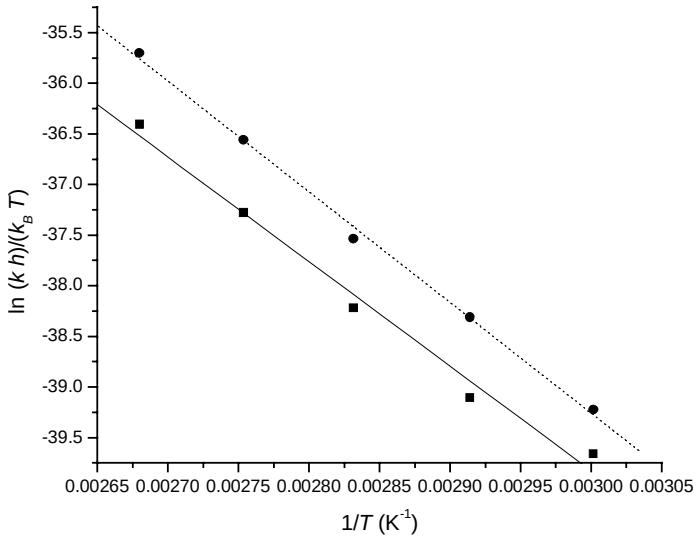


Figure S3. Eyring plots thermal helix inversion of (3*S*,3'*S*)-(*P*,*P*)-*trans*-**2** to (3*S*,3'*S*)-(*M*,*M*)-*trans*-**2** (solid line, squares) and (3*R*,3'*R*)-(*M*,*M*)-*trans*-**3** to (3*R*,3'*R*)-(*P*,*P*)-*trans*-**3** (dotted line, circles).

E Rotation Cycle for the Ethyl Substituted Molecular Motor (Details)

The racemate of the ethyl substituted molecular motor (3*R**,3'*R**)-(*P**,*P**)-*trans*-**3** was resolved into the enantiomers by preparative HPLC (Chiralpack OD, *n*-hexane : *i*-propanol = 99.9 : 0.1). The absolute configuration of the first eluted fraction was assigned to be (3*R*,3*R*')-(*P*,*P*)-*trans*-**3** by comparison with the CD spectra of the methyl substituted molecular motors (3*R*,3*R*')-(*P*,*P*)-*trans*-**1** and (3*S*,3*S*')-(*M*,*M*)-*trans*-**2**. The pseudo-enantiomeric relation between (3*R*,3*R*')-(*P*,*P*)-*trans*-**3** and (3*S*,3*S*')-(*M*,*M*)-*trans*-**2** can be seen clearly by comparison of the CD spectra of molecules, which are nearly mirror images. The second eluted fraction contained the (3*S*,3*S*')-(*M*, *M*)-*trans*-**2** enantiomer.

The UV-Vis and CD spectra of pure (3*R*,3*R*')-(*P*,*P*)-*trans*-**3** are depicted in Figures 14 and 15, respectively. The UV-Vis spectrum is characterized by three major absorption bands at 222, 236 and 320 nm. In the CD spectrum three important Cotton effects are observed at 217 ($\Delta\varepsilon$ = +145.8), 228 ($\Delta\varepsilon$ = +168.0) and 240 nm ($\Delta\varepsilon$ = -119.7). The rotary cycle was started with the irradiation of a solution in *n*-hexane of the stable (3*R*,3*R*')-(*P*,*P*)-*trans*-**3** isomer with axial methyl substituents ($\lambda \geq$ 280 nm, *T*= -60°C). When no further changes were observed in the UV-Vis spectrum and the PSS had been reached, UV-Vis and CD spectra were recorded. The UV-Vis and CD spectra observed during the rotary cycle are also depicted in Figures 14 and 15. After the irradiation, in the CD spectrum an overall inversion of the major Cotton effects was observed. Remarkable is the large increase in value of these Cotton effects found at 227.8 ($\Delta\varepsilon$ = -455.2) and 251.6 nm ($\Delta\varepsilon$ = +249.3). This inversion of the CD spectrum is indicative for the change in the helicity of the molecule going from an overall (*P*)-helicity in (3*R*,3*R*')-(*P*,*P*)-*trans*-**3** to an overall (*M*)-helicity in the newly formed isomer. From the UV-Vis and CD data it is concluded that this new isomer was the unstable (3*R*,3*R*')-(*M*,*M*)-*cis*-**3**. This (3*R*,3*R*')-(*M*,*M*)-*cis*-**3** has the ethyl substituents in an (pseudo-)equatorial orientation and is therefore thermally unstable, like the methyl substituted (3*S*,3*S*')-(*P*,*P*)-*cis*-**3** described in the previous paragraph. Heating of unstable

(3*R*,3*R'*)-(*M*,*M*)-*cis*-**3** was monitored by CD spectroscopy following the increase of the signal at 218 nm in time. When no further increase in the signal was observed, UV-Vis and CD spectra were recorded. As is especially clear from the CD spectrum in which the main absorptions have changed in sign, an overall inversion of the helicity of the molecule has taken place from unstable (3*R*,3*R'*)-(*M*,*M*)-*cis*-**3** with an overall (*M*)-helicity to an isomer with an overall (*P*)-helicity. It was concluded from UV-Vis and CD spectra in combination with comparison with material obtained from the synthesis that was characterized by HPLC and ^{1}H NMR, that stable (3*R*,3*R'*)-(*P*,*P*)-*cis*-**3** had been formed.

By monitoring this thermal helix inversion at various temperatures, the activation parameters of the process could be determined using the Eyring equation as has been demonstrated above. From the Eyring plot, the Gibbs energy ($\Delta^{\ddagger}G^{\theta}$ = 91±2 kJ·mol^{-1}), the enthalpy ($\Delta^{\ddagger}H^{\theta}$ = 79±1 kJ·mol^{-1}) and the entropy of activation ($\Delta^{\ddagger}S^{\theta}$ = -35±2 J·K^{-1}·mol^{-1}) of the process could be determined. The half-life of the conversion of (3*R*,3*R'*)-(*M*,*M*)-*cis*-**3** to (3*R*,3*R'*)-(*P*,*P*)-*cis*-**3** was then calculated from the Gibbs energy of activation and proved to be 18 min at room temperature (293.15 K). The samples used to determine the rate constants for the thermal helix inversion contain after the irradiation a small amount of stable (3*R*,3*R'*)-(*P*,*P*)-*trans*-**3**. The change in the CD spectra will, however, not be effected, since this is a thermally stable compound and hence does not have influence on the determination of the rate of the thermal helix inversion as was already explained for **2**. Since the composition of the mixture at the PSS state cannot be determined directly due to the instability of the unstable (3*R*,3'*R*)-(*M*,*M*)-*cis*-**3**, the sample was heated for several hours at 20°C to ensure complete conversion of (3*R*,3'*R*)-(*M*,*M*)-*cis*-**3** to (3*R*,3'*R*)-(*P*,*P*)-*cis*-**2.3**. The ratio between (3*R*,3'*R*)-(*P*,*P*)-*cis*-**3** relative to (3*R*,3'*R*)-(*P*,*P*)-*trans*-**3** then reflects directly the ratio between unstable (3*R*, 3'*R*)-(*M*,*M*)-*cis*-**3** and stable (3*R*,3'*R*)-(*P*,*P*)-*trans*-**3** at the PSS. The ratio between the two forms was determined by HPLC and proved to be 3:97. The sample obtained after the first two steps was then irradiated for the second time ($\lambda \geq$ 280 nm, *T*= -60°C). During the irradiation, the stable (3*R*,3'*R*)-(*P*,*P*)-*cis*-**3** isomer with axial methyl substituents was converted to the unstable (3*R*,3'*R*)-(*M*,*M*)-*trans*-**3** isomer with equatorial methyl substituents. The

process was again followed by UV-Vis and CD spectroscopy (Figures 14 and 15). Subsequent heating of the sample at 60°C converted in a slow process unstable (3*R*,3'*R*)-(*M*,*M*)-*trans*-**3** to stable (3*R*,3*R*')-(*P*,*P*)-*trans*-**3**. The ratio at the PSS of (3*R*,3'*R*)-(*P*,*P*)-*cis*-**3** and (3*R*,3'*R*)-(*M*,*M*)-*trans*-**3** was determined independently by irradiation of a sample of pure (3*R*,3'*R*)-(*P*,*P*)-*cis*-**3** ($\lambda \geq 280$ nm, T= -60°C). Since unstable *trans*-**3** is relatively stable compared to unstable *cis*-**3**, the PSS ratio (stable *cis*-**3**: unstable *trans*-**3** = 5:95) was determined directly by HPLC analysis. During the second thermal helix conversion, no thermodynamic data were acquired due to the relatively low rate of the process at 60°C and the volatility of the *n*-hexane used in the experiments. The photochemical properties of (3*R*,3'*R*)-(*P*,*P*)-*cis*-**3** are expected to be identical in dodecane and *n*-hexane. The higher boiling point of dodecane (180°C) is, however, suitable to determine the rate of the thermal helix inversion. Therefore, samples of pure (3*R*,3'*R*)-(*P*,*P*)-*cis*-**3** in dodecane were irradiated to give a mixture of stable (3*R*,3'*R*)-(*P*,*P*)-*cis*-**3** and unstable (3*R*,3'*R*)-(*M*,*M*)-*trans*-**3** at the PSS. Heating of the sample will result in a conversion of unstable (3*R*,3'*R*)-(*M*,*M*)-*trans*-**3** to stable (3*R*,3'*R*)-(*P*,*P*)-*trans*-**3**. The remaining stable (3*R*,3'*R*)-(*P*,*P*)-*cis*-**3** in the sample will remain unaffected and does not have influence on the determination of the rate of the thermal helix inversion. The Eyring plot, depicted above, was then used again to determine the Gibbs energy ($\Delta^{\ddagger}G^{\theta}$= 107±1 kJ·mol^{-1}), the enthalpy ($\Delta^{\ddagger}H^{\theta}$= 91±3 kJ·mol^{-1}) and the entropy of activation ($\Delta^{\ddagger}S^{\theta}$= -53±8 J·K^{-1}·mol^{-1}) of the process. The half-life of 317h at room temperature (T= 293.15 K) of the unstable *trans*-**3** isomer is, as expected, significantly longer than that of the unstable *cis*-**3**.

F Fluorescence Spectra

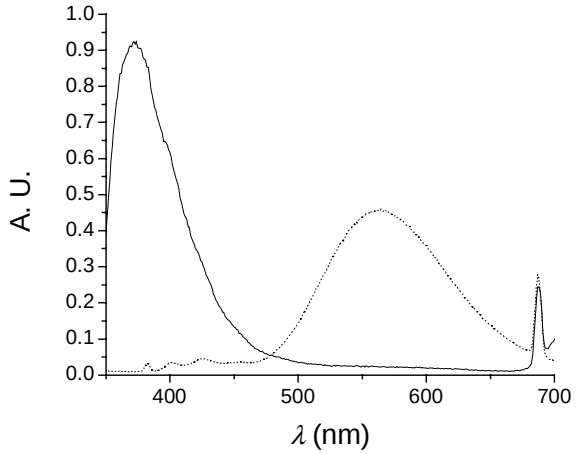


Figure S4. Fluorescence spectrum of (3*S*,3'*S*)-(*P*,*P*)-*trans*-**4** (solid line) and (3*S*,3'*S*)-(*M*,*M*)-*trans*-**4** (dotted line).

The conversion of the (3*S*,3'*S*)-(*P*,*P*)-*trans*-**4** to (3*S*,3'*S*)-(*M*,*M*)-*trans*-**4** could be monitored by measuring the decay of the fluorescence signal at λ= 374 nm of (3*S*,3'*S*)-(*P*,*P*)-*trans*-**4** or alternatively by measuring the increase of the fluorescence signal of (3*S*,3'*S*)-(*M*,*M*)-*trans*-**4** at λ= 568 nm. Detailed analysis of both fluorescence measurements revealed that during the irradiation going from (3*S*,3'*S*)-(*P*,*P*)-*trans*-**4** to (3*S*,3'*S*)-(*M*,*M*)-*trans*-**4** a first-order reaction not was followed.

G Mathematically Fitting the Thermal Helix inversion of *i*Pr-4

The conversion of the unstable (3*S**,3'*S**)-(*M**,*M**)-*trans*-**4** via (3*S**,3'*S**)-(*P**,*M**)-*trans*-**4** to (3*S**,3'*S**)-(*P**,*P**)-*trans*-**4** was followed in time by ^{1}H NMR as is depicted schematically below:

$$\left[M^{*}M^{*}{}_{trans}\right] \xrightarrow{k_1} \left[P^{*}M^{*}{}_{trans}\right] \xrightarrow{k_2} \left[P^{*}P^{*}{}_{trans}\right]$$

For ease of notation the following abbreviations are used:

$$\left[M^{*}M^{*}{}_{trans}\right] = x(t)$$

$$\left[P^{*}M^{*}{}_{trans}\right] = y(t)$$

$$\left[P^{*}P^{*}{}_{trans}\right] = z(t)$$

$$\mathrm{k}_1 = \mathrm{c}_1$$
$$\mathrm{k}_2 = \mathrm{c}_2$$

The entire process can be regarded as a homogeneous linear system with constant coefficients. For the process concerned, the following differential equations are involved giving the concentrations of *x* and *y* in time.

$$\frac{\partial x}{\partial t} = -\mathrm{c}_1 x(t)$$

$$\frac{\partial y}{\partial t} = \mathrm{c}_1 x(t) - \mathrm{c}_2 y(t)$$

When regarding the total amount of compound as one, the following statements are true:

$$z(t) = 1 - x(t) - y(t)$$

$$x(0) = 1$$

From this follows that the solution for $x(t)$ in time is:

$$\frac{\partial x}{\partial t} = -c_1 x(t)$$

$$x(t) = x(0)e^{-c_1 t}$$

The solution for $y(t)$ can be found by putting the equations in a vector form:

$$\begin{bmatrix} \frac{\partial x}{\partial t} \\ \frac{\partial y}{\partial t} \end{bmatrix} = \begin{bmatrix} -c_1 & 0 \\ c_1 & -c_2 \end{bmatrix} \begin{bmatrix} x(t) \\ y(t) \end{bmatrix}$$

From this matrix, the Eigenvalues ($-c_1$ and $-c_2$) and the following Eigenvectors were found:

$$\begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

$$\begin{bmatrix} \frac{c_2 - c_1}{c_1} \\ 1 \end{bmatrix}$$

Furthermore, the assumption is made that both equations have a logarithmic form so that the solutions can be written as follows:

$$\begin{bmatrix} x(t) \\ y(t) \end{bmatrix} = A \begin{bmatrix} \frac{c_2 - c_1}{c_1} \\ 1 \end{bmatrix} e^{-c_1 t} + B \begin{bmatrix} 0 \\ 1 \end{bmatrix} e^{-c_2 t}$$

Which gives for $x(t)$ together with the know solution (see above):

$$x(t) = \mathrm{A}\frac{\mathrm{c}_2 - \mathrm{c}_1}{\mathrm{c}_1}\mathrm{e}^{-\mathrm{c}_1 t} = x(0)\mathrm{e}^{-\mathrm{c}_1 t}$$

$$\mathrm{A} = x(0)\frac{\mathrm{c}_1}{\mathrm{c}_2 - \mathrm{c}_1}$$

For $y(t)$ then follows:

$$y(t) = \mathrm{A}\mathrm{e}^{-\mathrm{c}_1 t} + \mathrm{B}\mathrm{e}^{-\mathrm{c}_2 t}$$

$$y(0) = \mathrm{A} + \mathrm{B} = 0$$

$$\mathrm{B} = -x(0)\frac{\mathrm{c}_1}{\mathrm{c}_2 - \mathrm{c}_1}$$

$$y(t) = x(0)\frac{\mathrm{c}_1}{\mathrm{c}_2 - \mathrm{c}_1}\mathrm{e}^{-\mathrm{c}_1 t} - x(0)\frac{\mathrm{c}_1}{\mathrm{c}_2 - \mathrm{c}_1}\mathrm{e}^{-\mathrm{c}_2 t}$$

$$y(t) = x(0)\frac{\mathrm{c}_1}{\mathrm{c}_2 - \mathrm{c}_1}\left(\mathrm{e}^{-\mathrm{c}_1 t} - \mathrm{e}^{-\mathrm{c}_2 t}\right)$$

The complete solution that gives the concentration in time for all three compounds is therefore:

$$x(t) = x(0)\mathrm{e}^{-\mathrm{c}_1 t}$$

$$y(t) = x(0)\frac{\mathrm{c}_1}{\mathrm{c}_2 - \mathrm{c}_1}\left(\mathrm{e}^{-\mathrm{c}_1 t} - \mathrm{e}^{-\mathrm{c}_2 t}\right)$$

$$z(t) = 1 - x(t) - y(t)$$

That the solutions of $x(t)$ and $y(t)$ are correct can be seen by differentiation:

$$y(t) = x(0)\frac{\mathrm{c}_1}{\mathrm{c}_2 - \mathrm{c}_1}\left(\mathrm{e}^{-\mathrm{c}_1 t} - \mathrm{e}^{-\mathrm{c}_2 t}\right)$$

$$\frac{\partial y}{\partial t} = \frac{\partial\left(x(0)\frac{c_1}{c_2 - c_1}\left(e^{-c_1 t} - e^{-c_2 t}\right)\right)}{\partial t}$$

$$\frac{\partial y}{\partial t} = x(0)\frac{c_1}{c_2 - c_1}\left(-c_1 e^{-c_1 t} + c_2 e^{-c_2 t}\right)$$

$$\frac{\partial y}{\partial t} = x(0)\left(\frac{-c_1^2}{c_2 - c_1}e^{-c_1 t} + \frac{c_1 c_2}{c_2 - c_1}e^{-c_2 t}\right)$$

$$\frac{\partial y}{\partial t} = x(0)\left(\frac{-c_1^2}{c_2 - c_1}e^{-c_1 t} - \frac{c_1(c_2 - c_1)}{c_2 - c_1}e^{-c_1 t} + \frac{c_1(c_2 - c_1)}{c_2 - c_1}e^{-c_1 t} + \frac{c_1 c_2}{c_2 - c_1}e^{-c_2 t}\right)$$

$$\frac{\partial y}{\partial t} = x(0)\frac{c_1(c_2 - c_1)}{c_2 - c_1}e^{-c_1 t} + x(0)\left(\frac{-c_1^2}{c_2 - c_1}e^{-c_1 t} - \frac{c_1(c_2 - c_1)}{c_2 - c_1}e^{-c_1 t} + \frac{c_1 c_2}{c_2 - c_1}e^{-c_2 t}\right)$$

$$\frac{\partial y}{\partial t} = c_1 x(0)e^{-c_1 t} + x(0)c_1\left(\frac{-c_1}{c_2 - c_1}e^{-c_1 t} - \frac{(c_2 - c_1)}{c_2 - c_1}e^{-c_1 t} + \frac{c_2}{c_2 - c_1}e^{-c_2 t}\right)$$

$$\frac{\partial y}{\partial t} = c_1 x(t) + x(0)c_1\left(\frac{-c_1}{c_2 - c_1}e^{-c_1 t} - \frac{(c_2 - c_1)}{c_2 - c_1}e^{-c_1 t} + \frac{c_2}{c_2 - c_1}e^{-c_2 t}\right)$$

$$\frac{\partial y}{\partial t} = c_1 x(t) + x(0)\frac{c_1}{c_2 - c_1}\left(c_1 e^{-c_1 t} - (c_2 - c_1)e^{-c_1 t} + c_2 e^{-c_2 t}\right)$$

$$\frac{\partial y}{\partial t} = c_1 x(t) + x(0)\frac{c_1}{c_2 - c_1}\left(c_2 e^{-c_2 t} - c_2 e^{-c_1 t}\right)$$

$$\frac{\partial y}{\partial t} = c_1 x(t) + c_2 x(0)\frac{c_1}{c_2 - c_1}\left(e^{-c_2 t} - e^{-c_1 t}\right)$$

$$\frac{\partial y}{\partial t} = c_1 x(t) - c_2 x(0)\frac{c_1}{c_2 - c_1}\left(e^{-c_1 t} - e^{-c_2 t}\right)$$

$$\frac{\partial y}{\partial t} = c_1 x(t) - c_2 y(t)$$

Applying different constant and fitting with the experimental data gave for $k_1 = 1.0 \cdot 10^{-4}$ s^{-1} and $k_2 = 1.1 \cdot 10^{-5}$. Applying these rate constants gave for the conversion of (3*S**,3'*S**)-(*M**,*M**)-*trans* **4** to (3*S**,3'*S**)-(*P**,*M**)-*trans* **4** a Gibbs energy of $\Delta G^{\ddagger} = 124$ kJ·mol^{-1} at $T = 383.15$K. For the conversion of (3*S**,3'*S**)-(*P**,*M**)-*trans* **4** to (3*S**,3'*S**)-(*P**,*P**)-*trans* **4** using the same methodology, a value of 131 kJ·mol^{-1} at $T = 383.15$K was found.

H References

1. Villiers, C.; Vandais, A.; Ephritikhine M. *J. Organomet. Chem*. **2001**, *617-618*, 744-747; b) Villiers, C.; Ephritikhine, M. *Chem. Eur. J.* **2001**, *7*, 3043; c) Villiers, C.; Ephritikhine, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2380-2382.
2. a) Wiel, M. K. J. ter; Koumura, N.; Delden, R. A. van; Meetsma, A.; Harada, N.; Feringa, B. L. *Chirality*, **2000**, *12*, 734-741; b) Wiel, M. K. J. ter; Koumura, N.; Delden, R. A. van; Meetsma, A.; Harada, N.; Feringa, B. L. *Chirality*, **2001**, *13*, 336.
3. In this context “plane naphthalenes” indicates the angle between the least-square planes of both naphthalene moieties in the molecule.